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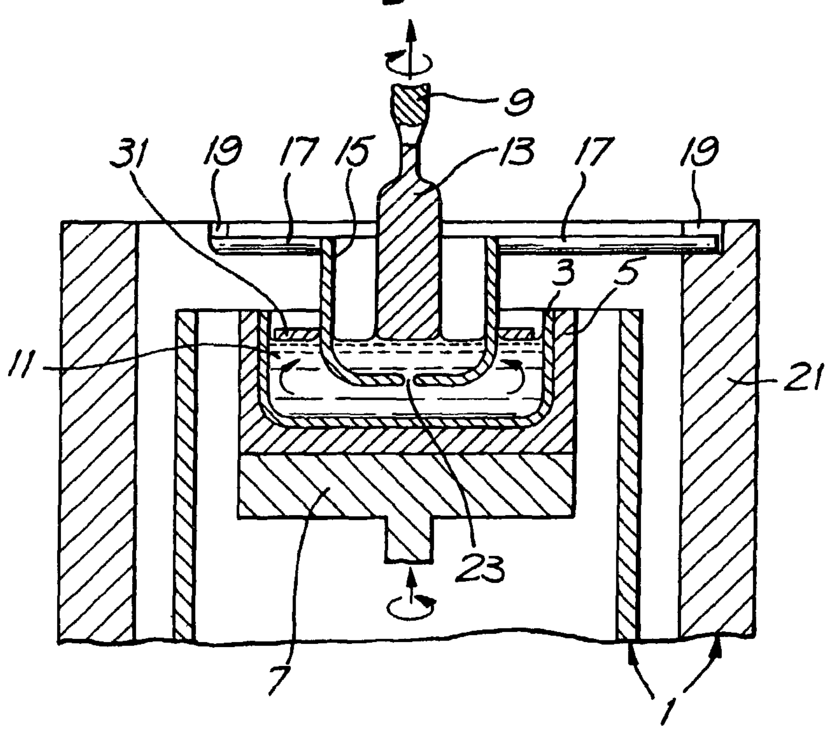
(54) Method and apparatus for crystal growth

(57) A modified method and apparatus for Czochralski crystal growth in which fluctuations in dopant concentration and in growth temperature are reduced by using an open baffle (15) of relatively inert material mounted concentric with furnace bore (21) in stationary position whilst the growing crystal (13) and containing crucible (15) are rotated. The baffle (15) may be in the form of a right circular hollow cylinder or in the form of a perforate crucible. When applied to the growth of silicon crystal (13) it is preferable that the baffle (15) is of silica material. In this case it may be arranged that oxide eroded by flow of melt through the apertures of the perforate crucible is introduced into the melt to replenish and maintain the oxygen content of the melt adjacent the growing crystal (13).

Fig. 1.



The drawings originally filed were informal and the print here reproduced is taken from a later filed formal copy.

Fig.1.

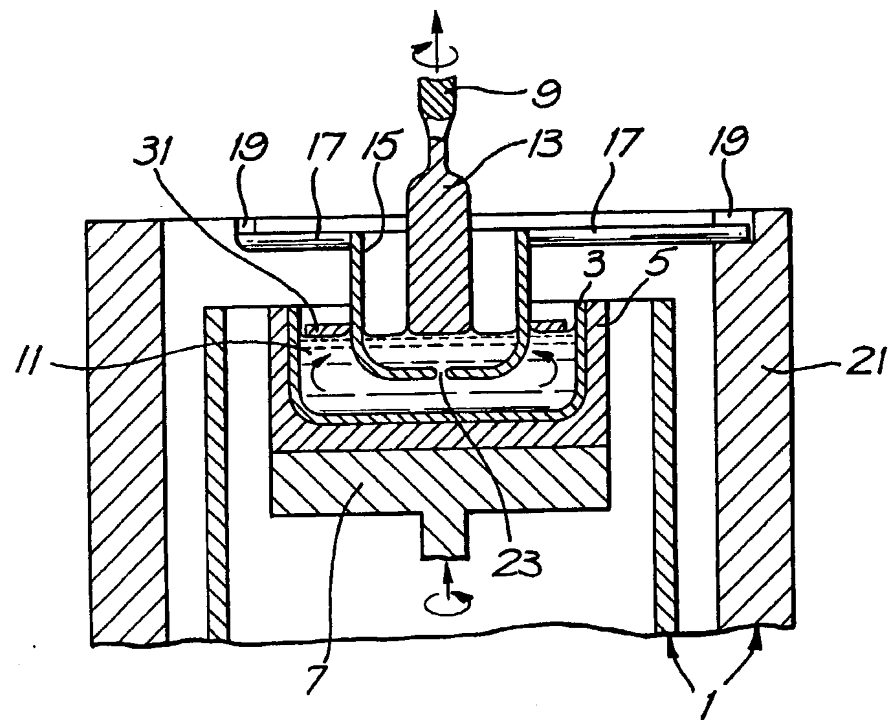
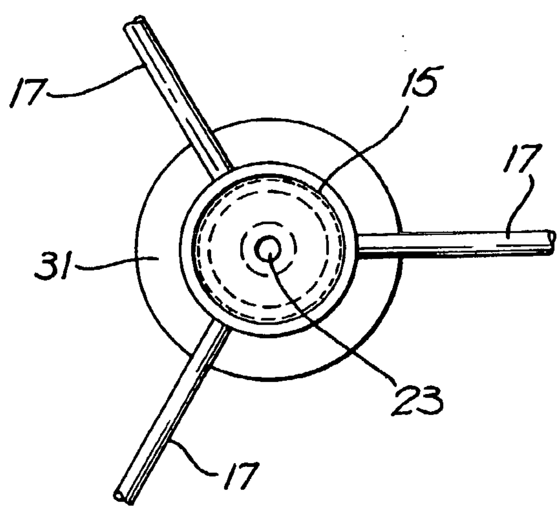


Fig.2.



SPECIFICATION

Method and apparatus for crystal growth

The present invention relates to crystal growth by the Czochralski technique, and concerns in particular an improved method and apparatus for performing the same.

In conventional application of the Czochralski technique, a seed crystal is lowered into contact with a melt of the same material and is rotated and slowly withdrawn at a controlled rate. After an initial period of controlled growth during which the pulled crystal is flared out to a desired diameter, the pulling rate and melt temperature are controlled to maintain the diameter within predetermined limits. The melt is contained in a crucible of relatively inert, high purity, material, eg in the case of silicon crystal growth, a crucible of fused silica (SiO_2) is used. Quite often this crucible is raised inside the furnace as the crystal is pulled, in order to maintain the liquid level at a constant position relative to the furnace and thus avoiding problems arising from changing temperature gradient, as the crystal is grown. During growth, heater current is varied to correct temperature drift, and these corrections may be modified to minimise the latent effects of thermal lag, ie the lag between the time heating correction is applied and the time the temperature at the crystal/melt interface is changed in response (see for example UK Patent No 1,478,192). For this purpose heating control may respond to photosensors positioned to monitor the crystal diameter, or to transducers monitoring the weight or inertial mass of the crystal or of the melt. (See also UK Patent Nos 1,434,527; 1,457,275; 1,465,191 and 1,494,342.)

In the case of silicon it is necessary to support the crucible in robust carbon liners, and these are normally slotted to allow for crucible expansion. Unfortunately, this often results in an assymetry in the thermal field. To compensate for this it is usual to introduce a relative rotation between the pulled crystal and the crucible, the crystal is rotated about the pulling axis, the crucible is usually rotated in the opposite direction. As well as preventing assymetrical growth outwards from the crystal, this also produces a forced convection in the melt, and in small scale apparatus this may be sufficient to obviate problems arising from thermal convection. However, on a microscopic scale, both rotational and non-rotational dopant striations (compositional fluctuations) are found to result, and present a problem particularly where crystals of high quality are needed.

On a macroscopic scale it is also a problem producing uniformly doped crystals. Because of the different dopant solubility in solid and liquid, dopant is rejected at the crystal/melt interface and can result in dopant concentration in the melt if segregation coefficient is <1. As a result, the dopant distribution in the pulled crystal exhibits longitudinal variation. To solve this problem a floating crucible technique has been adopted. (See for example J Applied Phys, *29*, (1958) p 1241). According to this technique, an inner crucible is mounted in sliding contact within the container crucible. Dopant is introduced into the inner crucible. As this dopant is rejected at the crystal melt interface, dilute melt is drawn into the inner crucible through a small hole in the crucible wall, to maintain constant dopant proportion. Without further introduction of suitable inserts or fenders, this technique is not readily applicable to the growth of silicon because of the stiction that occurs between the inner and outer silica crucibles. Rotational striations are also found to result.

Further problems arise where scaled up apparatus is used to produce crystals of large diameter (ie $>2''$ (5 cm) dia). The thermal driving force for convective flow - this is proportional to the cube of the crucible radius - is increased to such extent that compensation by forced convection, that resulting from the crystal and crucible rotations, becomes inadequate. The resulting thermal convection currents perturb the localised growth rate and diffusion boundary layer thickness which result in respectively non-rotational striations and large macroscopic variations in the radial distribution of dopants and impurities (eg interstitial oxygen).

There is a need for quantity production of high quality silicon crystals to meet the demands of VLSI technology, a need not readily met by the existing techniques referred to above.

The present invention is intended to provide a remedy. In particular it is intended to;

(i) reduce rotational and non-rotational dopant striations

(ii) improve macroscopic radial distribution of dopant. In this case 'dopant' may be a deliberately added electrically active impurity or an impurity arising from the melt or crucible (eg carbon and oxygen in silicon)

(iii) In the case of silicon, to improve the longitudinal variation of interstitial oxygen by maintaining it at a high level, characteristic of the seed-end part of the crystal.

According to the invention there is provided a method of growing a crystal of semiconductor material including: introducing a seed crystal into contact with a melt and withdrawing it at a controlled rate and temperature to maintain the diameter of the pulled crystal within predetermined limits, the melt being contained within a crucible disposed in the bore of a cylindrical furnace, the crucible being raised relative to the furnace to maintain the melt at a constant level and rotated, the pulled crystal and the crucible being rotated about the pulling axis; wherein, an open baffle of relatively inert material and of annular cross-section is held stationary and centred relative to the furnace and is interposed between the growing crystal and the wall of the crucible.

Since the crucible and melt rotate relative to the baffle, and the baffle is of annular cross-section and lies between the pulled crystal and the crucible wall, the baffle tends for typical rotation rates, to smooth spatial temperature variation to reduce assymetry in the thermal field in the vicinity of the crystal/melt interface. Furthermore, the baffle impedes thermal convection flow within the crucible. It therefore tends to reduce

thermal convection currents in the immediate vicinity of the crystal/melt interface. It therefore tends to reduce both the non-uniform nature of the thermal convection currents at different points of the crystal/melt interface (radial segregation effects) and the unsteady time-dependent thermal convection which leads to transient effects (non-rotational striations).

Apparatus for performing the above method comprises:-

a furnace having a cylindrical bore;

a container crucible of relatively inert material supported within the bore and held concentric with the bore; a lift mechanism supporting the crucible, for raising and rotating the crucible; a pulling mechanism for withdrawing a growing crystal from melt contained in the crucible, and for rotating the crystal about an axis concentric with the bore;

first control means for co-ordinating crystal pull and crucible lift to control the melt level relative to the furnace;

second control means for controlling growth temperature; and,

and open baffle of relatively inert material, of annular cross-section, mounted concentric with the bore in stationary position relative to the furnace, where it can be interposed between the growing crystal and the crucible wall.

The baffle may be in the form of a right circular hollow cylinder, open at its lower extremity. In preference to this, it may be in the form of a perforate crucible, the one or more apertures in the wall thereof being of sufficient size as to permit equalisation of melt level inside and out when the container crucible is raised. The apertures may be in the form of holes or slots. It is, in this case, a further advantage that the perforate crucible may be readily drained of melt upon lowering of the container crucible, and after slow cooling it can be retained for repeated use.

An example of one way of carrying out the invention is described in detail below with reference to the accompanying drawings in which:-

Figure 1 is a cross-section view of apparatus embodying the features of the invention; and,

Figure 2 is a plan view of the perforate crucible included in this apparatus.

There is shown in Figure 1 an apparatus for growing a crystal by the Czochralski technique, comprising, in its basic design, an electrical resistance furnace 1 having a cylindrical bore in which there is concentrically located a container crucible 3. This crucible is supported by a graphite liner 5 upon a rotatable lift assembly 7. There is also a rotatable crystal pull assembly 9 located on axis above the container crucible 3. This apparatus also includes servo-mechanisms (not shown) for monitoring crystal growth (eg weight sensors or photosensors, heater and mechanism controls), for controlling and co-ordinating the pull and lift rates to control the level of melt 11 in the container crucible 3 relative to the furnace 1, and for controlling growth temperature of the crystal 13.

For growing silicon crystals nominally of 3" (7.5 cm) diameter, the following apparatus/process parameters may be adopted:-

Growth rate 3.5 inches (8.9 cm) per hour, <100> silicon
Crystal rotation 15 rpm, clockwise,
Crucible rotation 8 rpm, counter-clockwise
Furnace atmosphere: high purity argon at 20 torr
Container crucible: 8" (20 cm) diameter, 6" (15 cm) high of fused silica

Consistent with the invention, the apparatus has been modified by the introduction of an open baffle 15, mounted concentric with the bore of the furnace 1. As it is shown in the Figures, it is in the form of a perforate crucible of transparent, high-purity fused silica and is supported by silica rods 17 extending outwards from its top extremity at 120° to each other. The crucible support rods 17 are welded onto the sides of the silica crucible 15 and when located in drilled recesses 19 in the furnace housing 21, constrain it to lie stationary in correct position in the furnace 1, concentric with the pulling axis and furnace bore. The rods 17 may be arched, if necessary, to allow for the upward displacement of the container crucible 3. In this example the perforate crucible 15 is of 6" (15 cm) diameter and has a single hole 23 of 7/16" (1 cm) diameter at its centre.

This apparatus is used as follows:- firstly a charge of high purity silicon is loaded into the container crucible 3. The perforate crucible 15 is then lowered into its correct position, rods 17 located in the grooves 19 of the furnace housing 21. Prescribed quantities of dopant - eg high purity aluminium - may be loaded into the two crucibles 3, 15 at this stage. The apparatus is evacuated and argon introduced at the desired flow rate and pressure. The furnace 1 is brought to operating temperature, the charge of silicon and dopant allowed to melt and the container crucible 3 raised until the level of melt 11 is at the desired position relative to the furnace 1. This must be done slowly to avoid any undue strain on the perforate crucible 15 that would dislodge it from its location or would plastically deform its shape. Growth is initiated upon lowering an oriented crystal seed into contact with the melt 11. The temperature is adjusted to establish optimum seed-on conditions and, after allowing time for the temperature to equilibrate, the seed pull rate is adjusted to allow growth of a thin neck of silicon at a high growth rate (eg 6 iph) sufficient to grow out all glissile dislocations (many of these are produced from the initial thermal shock of contact), to produce a dislocation-free material. Small manual changes of melt temperature are made to maintain the required crystal neck diameter. After approximately 3" (7.5 cm) of neck growth the temperature and seed pull rate are reduced to flare out the dislocation-free crystal rapidly to full diameter - as in the conventional process. When the crystal diameter has reached $\sim$ 3" (7.5 cm) the seed pull rate is first rapidly increased and the

temperature reduced further to reduce the flare and maintain the diameter just above 3" (8.0 cm). Once the diameter has stopped changing from this desired value the seed pull rate is reduced to near the desired rate of 3.5 inches per hour (8.9 cm ph) and the crucible lift rate accurately set at approx 0.5 iph (1.2 cm ph) to maintain the melt level in the same position. Temperature adjustments are then made and the servo-mechanisms switched to provide automatic diameter control. Once the desired length of crystal, and end-taper, have been grown, the crystal 13 is lifted from the melt and the container crucible 3 lowered slowly - eg at 0.5" (1.2 cm) per hour - so that all the silicon melt 11 is gradually transferred into the container crucible 3 without solidifying in the perforate crucible 15 (which would inevitably cause cracking due to the large expansion of silicon on solidification). The melt temperature is also increased. Finally the perforate crucible 15 is left in the furnace 1 and the furnace 1 allowed to cool slowly. The perforate crucible 15 is then removed, blasted with alumina particles to remove all tenacious silicon monoxide deposits, chemically cleaned, rinsed in de-ionised water and dried in preparation for further use.

The following experimental results have been found for an aluminium, p-type silicon crystal grown by the above technique, compared with similarly-doped crystals grown under control conditions without the inner crucible baffle 15:-

TABLE OF RESULTS:

		Crystal Grown WITH BAFFLE	Crystal Grown WITHOUT BAFFLE
INTERSTITIAL OXYGEN UNIFORMITY			
a)	Longitudinal Gradient	0.5×10^{18} at cm^{-3}	1.125×10^{18} at cm^{-3}
b)	Seed-end value	$\sim 1.8 \times 10^{18}$ at cm^{-3}	$\sim 1.8 \times 10^{18}$ at cm^{-3}
c)	Tail-end value (50% of 5 kg charge pulled)	$\sim 1.5 \times 10^{18}$ at cm^{-3}	$\sim 1.15 \times 10^{18}$ at cm^{-3}
d)	Radial gradient at seed-end	5-10%	15-20%
e)	Radial gradient at tail-end	6-9%	10-20%
SUBSTITUTIONAL DOPANT (Al) UNIFORMITY			
a)	Rotational striations (microscopic resistivity variation)	Some detected in certain sections on outer edge but << 7% resistivity (peak-peak) variations	Always present in outer edge giving 16-20% peak to peak variation in micro-resistivity
b)	Radial Resistivity (macroscopic resistivity variations)	<< 110% nearer 5% variation	10% dip

It can be seen from these results that both the oxygen and substitutional dopant uniformity have been improved by the new process. This improved uniformity in oxygen is believed to be due to the constant erosion of the stationary inner crucible 15 by the forced flow of silicon melt 11, according to the reaction:

$$\underset{\text{(melt)}}{Si} + SiO_2 \rightarrow \underset{\text{(solution)}}{2SiO} \rightarrow \text{into crystal.}$$

This reaction also occurs in the conventional pulling process but in this case since the liquid is rotating with the container crucible 3 the reaction is readily slowed down by the build-up of SiO on the walls of the

container crucible 3. Also, as pulling proceeds and the melt level in the container crucible drops, the driving force for thermal convection decreases and the crucible erosion rate is further reduced. The mechanism for losing oxygen from the apparatus by surface evaporation remains constant, during the process, however, assuming that the crucible 3 and crystal 13 have constant diameters. In the conventional process, therefore, a decrease in oxygen concentration from seed to tail results, whereas in the modified process the tail-end oxygen concentration is increased so to remain within ~ 20% of that at the seed-end (see Table).

Oxygen loss at the surface of the melt 11 may be minimised by covering the annulus of melt between the two crucibles 3, 15 with high purity silica powder or with a solid lid annulus 31 of silica, attached to the inner crucible. Sufficient clearance is provided between this lid 31 and the wall of the container crucible 3 to avoid stiction. As well as reducing evaporation of SiO this has the added benefit of reducing heat loss and therefore conserves electrical power too.

CLAIMS

1. A method of growing a crystal of semiconductor material including:
introducing a seed crystal into contact with a melt and withdrawing it at a controlled rate and temperature to maintain the diameter of the pulled crystal within predetermined limits. The melt being contained within a crucible disposed in the bore of a cylindrical furnace the crucible being raised relative to the furnace to maintain the melt at a constant level and rotated, the pulled crystal and the crucible being rotated about the pulling axis; wherein, an open baffle of relatively inert material and of annular cross-section is held stationary and centred relative to the furnace and is interposed between the growing crystal and the wall of the crucible.

2. A method of growing a crystal of semiconductor silicon material including:
introducing a seed of silicon crystal into contact with a melt of silicon and withdrawing it at a controlled rate and temperature to maintain the diameter of the pulled crystal within predetermined limits, the melt being contained within a crucible disposed in the bore of a cylindrical furnace, the crucible being raised relative to the furnace to maintain the melt at a constant level and rotated, the pulled crystal and the crucible being rotated about the pulling axis; wherein an open baffle provided by a perforate crucible of erodible silica material is held stationary and centred relative to the furnace and is interposed between the growing crystal and the wall of the crucible, wherein furthermore the oxygen content of the melt contained within the perforate crucible is replenished and maintained by erosion of the silica material as melt is forced to flow into the perforate crucible through the one or more apertures thereof.

3. A method of growing a crystal of semiconductor silicon material performed substantially as described hereinbefore.

4. Apparatus for performing the method claimed in Claim 1 above the apparatus comprising;-
a furnace having a cylindrical bore;
a container crucible of relatively inert material supported within the bore and held concentric with the bore;
a lift mechanism supporting the crucible, for raising and rotating of the crucible;
a pulling mechanism for withdrawing a growing crystal from melt contained in the crucible, and for rotating the crystal about an axis concentric with the bore;
first control means for co-ordinating crystal pull and crucible lift to control the melt level relative to the furnace;
second control means for controlling growth temperature; and
an open baffle of relatively inert material, of annular cross-section, mounted concentric with the bore in stationary position relative to the furnace, where it can be interposed between the growing crystal and the crucible wall.

5. Apparatus as claimed in Claim 4 above wherein the baffle is in the form of a right circular hollow cylinder open at its lower extremity.

6. Apparatus as claimed in Claim 4 above wherein the baffle is in the form of a perforate crucible, the one or more apertures in the wall thereof being of sufficient size as to permit equalisation of melt level inside and out when the container crucible is raised.

7. Apparatus as claimed in Claim 6 above wherein the one or more apertures are disposed such as to permit the draining of all melt from the perforate crucible.

8. Apparatus as claimed in Claim 4 above wherein above the base of the baffle there extends from the external periphery thereof an annular solid lid, this lid being constructed to extend towards but to lie just clear of the wall of the container crucible when the container crucible is in raised position.

9. Apparatus constructed, arranged and adapted to perform substantially as described hereinbefore with reference to and as shown in Figures 1 and 2 of the accompanying drawings.

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